COLLISIONAL LINE SHIFTS OF CO2 AND THEIR INFLUENCE ON THE PROPAGATION OF THE CO2–LASER RADIATION THROUGH THE ATMOSPHERE

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The results of measurements of the collisional line shifts of CO_2 for air and *pure gas in the bands centered at* 1.4, 2.7, 4.3. 4.8, 9.0, 9.4, *and* 10.6 μm *are presented. The line shift coefficients lie within the interval from* 0 *to* $\pm 0.025\ cm^{-1}\ atm^{-1}$. *The influence of the collisional line shifts on the propagation of the* CO_2*–laser radiation through the atmosphere is estimated. It is shown that the line shift can cause the increase in monochromatic transmission of the vertical atmospheric column almost twice for separate lasing frequencies.etc.*

The interest to the data on collisional line shifts in the band centers is caused not only by the needs of molecular and laser physics but also by the needs of a number of applied aspects of atmospheric optics. The collisional shifts of the absorption lines of atmospheric gases as well as their half–widths that are determined by the type of the intermolecular interaction have been already studied for a long time. [1,2] In recent years the lines shifts of water vapor are investigated most thoroughly,[3–5] since they have a marked effect on the accuracy of solving the inverse problems of lidar sensing of the atmosphere (see, e.g., Ref. 6).

At the same time, the data on collisional line shifts of CO_2 is much scanty. The line shifts of CO_2 were measured mainly using the laser spectroscopy techniques, the measurements is aimed mostly at improving the accuracy of secondary standards of transition frequencies in the IR region[7–9] as well as at correction for systematic error in ranging with laser range–finders.[10] Normally the line collisional shifts, in the band 9.4 ... 10.6 μm at low pressures ($P \le 10^{-4}$ atm) were investigated At pressure values close to the atmospheric, the line shifts in the bands around 1.4 μm (Refs. 11 and 12) and 9.4 μm (Ref. 13) of CO_2 in the presence of collisions with He were measured. The line shift coefficients obtained in these works significantly exceeded the coefficients obtained at low pressures. Moreover, it often happened that the sign of line shift due to pressure was opposite. As was shown in Ref. 14 the line shift coefficient $\beta = \Delta\nu_L/P$ can vary when the pressure is changed over a sufficiently wide range. Thus, for example, the line shift coefficient $\beta_{CO_2-CO_2}$ in the absorption band around 10.6 μm being $(1.57 \pm 0.46) \cdot 10^{-3}\ cm^{-1} \cdot atm^{-1}$ at $P \le (3–4) \cdot 10^{-4}$ atm was found to be $-(2 \pm 1.3) \cdot 10^{-3}\ cm^{-1} \cdot atm^{-1}$ at pressure P being equal to about 0.01 atm.

The data on the line shift coefficient at pressures $P \le 1$ atm are necessary for solving the atmospheric optics problems. We present the results of measuring the collisional shifts of the CO_2 lines obtained by the authors earlier.[15] The measurements have been made in the bands centered at 1.4, 2.7, 4.3, 4.8, and 9.6 μm for air and pure CO_2. The effect of these line shifts on propagation of the CO_2–laser radiation has been also estimated here.

MEASUREMENT TECHNIQUE AND INSTRUMENTATION

Measurements of line collisional shift coefficients are not so simple in performance, because of very small values of these coefficients (normally $\beta \le 0.02\ cm^{-1} \cdot atm^{-1}$). Usually, only unique laser spectrometer and Fourier spectrometer is used for such measurements. In our experiment we used the computer–controlled setup which included a conventional double–pass 5 m–focal length diffraction spectrometer (the Litthrow scheme) described elsewhere,[16] and an automated 15 VUMS 28–025 signal recording system, based on an Elektronika–60 computer (a version of a PDP 11/70 computer).

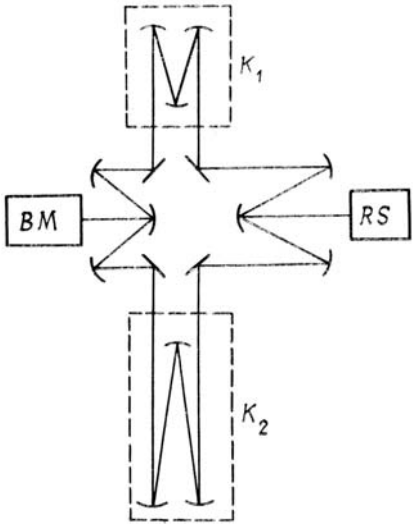

FIG. 1. Schematic diagram of the experimental arrangement

We used a ceramic metal rod with a brightness temperature about 1320 K as a source of radiation with continuous spectrum and a deep-frozen bolometer[17] with the following specifications: the temperature in cryostat 4.23 K, the receiving area 0.7 x 7.0 mm,^{2} the noiseequivalent power at

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a modulation frequency of 18.75 Hz about $1.8 \cdot 10^{-12}$ W · Hz$^{1/2}$, the gain about 1000, and theoretical resolution of the spectrometer 0.02 cm^{-1} — as a radiation receiver.

The differential technique used for measurements of the line collisional shifts (see Fig. 1), was as follows. Monochromatic radiation emanating from the basic monochromator (BM) was alternately transmitted with the help of an optical beam splitter through either multipass gaseous cell K_1 or K_2 and then was fed into the recording system (RS). One of the cells contained an absorbing gas whose lines were shifted and broadened due to its own pressure or pressure of the buffer gas (total pressure $P_t \simeq 1$ atm), and the second contained a gas at low pressure ($P = 10^{-3} - 10^{-2}$ atm). Provided a fixed position of the dispersive elements in step–scanning we recorded, by turns, the light passed alternately through either cells. Measuring these two signals successively at different frequencies during one scanning leads to two spectral line profiles, one being displaced with respect to the other. If the displacement in steps of the scanning element (detector array or encoder) and the step size are known (the encoder was operated with a scanning step of $(1–2) \cdot 10^{-3}$ cm^{-1}), the line shift due to pressure can be easily found. In order to increase the signal–to–noise ratio up to 200–300, the detected signal was integrated for each spectral position during several minutes. From a comparison of line profiles obtained at equal pressures in both cells we determined the systematic errors due to the errors in the instrument adjustment, which then were taken into account when determining the line shifts in the band centers. The error in measuring the line shifts was approximately equal to the scanning step size ~ 0.002 cm^{-1}.

MEASUREMENT RESULTS

In the experiments we have measured the shifts of individual CO_2 absorption lines both for selfbroadening (CO_2–CO_2 interaction) and broadening by air molecules. For measurements we selected the lines with the minimal overlapping of the adjacent lines. Really, the asymmetry of a line profile caused by overlapping can be mistaken for the line collisional shifts. The spurious line shifts determined from the model calculations for the lines chosen, did not exceed 0,001 cm^{-1}. Table I shows the results of measurements for individual lines in the bands centered at 1.4, 2.7, 4 3, 4,8, and 10.6 μm, and Fig. 2 shows the results for the lines in the band around 9.4 μm for broadening by air molecules.

As a rule, the dependence between the line shift and the rotational state of an absorbing molecule is low, however, in contrast to the spectral line half–width, the line shift significantly changes with the vibrational state of the absorbing molecule. The line shift in the R–branch of the band centered at 9.4 μm for broadening by air molecules are a little bit larger than those in the P–branch, in addition the line shift oscillations become noticeable in both branches. Such a dependence has been observed earlier in Ref. 18 in the case of polar molecules. The line shift coefficients in the case of "self–shift" due to collisions between CO_2 molecules were determined for individual lines in the P– and R–branches of the band centered at 10.6 μm. In particular, for the line $P20$ the line shift coefficient is $\beta_{CO_2-CO_2} = -0.002 \pm 0.002$ cm^{-1} · atm^{-1}. This value is close to the values $\beta < -2.5 \cdot 10^{-3}$ cm^{-1} · atm^{-1} $\beta = -(2.5 \pm 1.3) \times 10^{-3}$ cm^{-1} · atm^{-1} at $P \le 1.3 \cdot 10^{-2}$ atm, which have been published earlier in Refs. 8 and 14, while it is substantially different from the value $\beta = -(8.8 \pm 1.5) \times 10^{-3}$ cm^{-1} · atm^{-1} at $P \le 8 \cdot 10^{-5}$ atm, which has been obtained in Ref. 8.

TABLE I. Line shift coefficients of CO_2 (cm^{-1}atm^{-1}).

Band center	Line	β_{CO_2-air}	$\beta_{CO_2-CO_2}$
1.4 μm	R(4)		− 0.005 ± 0.001
	RIO		− 0.007 ± 0.001
	P18		− 0.012 ± 0.001
	P4		− 0.012 ± 0.001
	P10		− 0.012 ± 0.001
	P14		− 0.011 ± 0.002
2.7 μm	RO	+ 0.010 ± 0.003	
	R14	− 0.014 ± 0.003	
	R34	− 0.015 ± 0.003	
	P2	+ 0,011 ± 0. 003	
	P36	+ 0.017 ± 0.003	
4.3 μm	P56		− 0.012 ± 0.002
	P60		− 0.013 ± 0.002
4.8 μm	P26	+ 0.027 ± 0.003	
10.6 μm	R4		− 0 007 ± 0.002
	R20		+ 0.004 ± 0.002
	R44		+ 0.009 ± 0.002
	P4		− 0.009 ± 0.002
	P12		0.0 ± 0.002
	P18		0.0 ± 0.002
	P20		− 0.002 ± 0.002

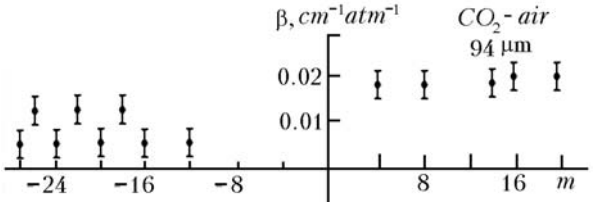

FIG. 2 Measured values of the collisional shift coefficient of CO_2 *in the band centered at* 9.4 μm.

Our results for the band centered at 1.4 μm disagree with the experimental and theoretical data presented in Ref. 12. Thus, the calculations made in Ref. 12 showed that the line shift coefficient changes from − 0.010 to − 0.015 cm^{-1} · atm^{-1} as $|m|$ increases from 5 to 35, and according to Ref. 12 the shift coefficient measured for the line $R6$ (averaged over the band) was about − 0.014 ± 0.004 cm^{-1} · atm^{-1}. Our data indicates that the average shift coefficient for $4 < |m| < 18$ is about −0.010 ± 0.02 cm^{-1} · atm^{-1}.

INFLUENCE OF THE LINE SHIFT ON THE PROPAGATION OF THE CO_2–LASER RADIATION THROUGH THE ATMOSPHERE

The line shifts discovered in the bands 9.4 . . . 10.6 μm is of dramatic importance for calculating the propagation of the laser radiation through the atmosphere. Really, in this case it is necessary to examine not only the shifts in the band centers of resonance absorption lines of CO_2 depending on the pressure along the propagation path, but also the shifts in the band centers of lasing lines of the CO_2 laser depending on the pressure and composition of an active medium. As a result, the final effect will be determined by the atmospheric absorption spectra in the vicinity of lasing frequency.

To make quantitative estimates of this effect we performed a series of computer calculations by the "direct" method based on the data bank on the parameters of the

absorption lines of atmospheric gases.[20] We calculated transmission of radiation along the vertical atmospheric paths extended from a certain altitude z up to the upper boundary of the atmosphere. We also calculated the values of monochromatic absorption coefficients for different altitudes for the main absorbing components of the atmosphere. We considered two versions of the problem — one with account of the shifts of lasing lines of laser (the CO_2 lasers at low pressure) and the other without account of such line shifts.

In the case of the low pressure lasers the line shift in the absorption band center of atmospheric CO_2 with respect to the lasing frequencies has maximum value in the surface layer of the atmosphere since it is proportional to air pressure. The line shift coefficient in this case is, according to Table I, about 0.006...0.02 cm^{-1}. Since the half–widths of the atmospheric absorption lines of CO_2 in the surface layer of the atmosphere is about 0.1 $cm^{-1} \cdot atm^{-1}$, then evidently the monochromatic absorption coefficients vary insignificantly. Really, even for lines with the line shift coefficients of the order of 0.02 $cm^{-1} \cdot atm^{-1}$ the decrease of the absorption coefficient will be less than 10% in the surface layer of the atmosphere and 5–6% at an altitude of 10 km. As a result, the transmission of vertical paths varies only slightly: for the paths extended from the ground level by some fractions of percent and by 1–1.5% for the paths extended from z = 10 km.

Quite different situation we have when the active medium is at a pressure comparable with the atmospheric pressure. In this case the line collisional shifts can lead to more significant changes in the atmospheric absorption. The sign of the lasing line shift with respect to the shift of an absorption line is of dramatic importance. Thus, if the signs of line shifts coincide, then the separation between the lines in band centers will be minimal in the atmospheric surface layer and will increase with height. Since the absorption lines in the upper atmosphere are narrow, the change in the absorption coefficient will be more significant. It is clear that the effect will be more pronounced if the signs of shifts are opposite.

To evaluate the effect of the lasing line shifts, one needs for the data on the line shift coefficients of the gases which compose the active medium. Assuming that the line shifts due to the collisions of the CO_2 molecules with the N_2 and air molecules are of the same value and using $\beta_{CO_2-He} = -9.8 \cdot 10^{-3}$ $cm^{-1} \cdot atm^{-1}$ determined in Ref. 1 for the line $P20$, one can estimate, based on the data from Table I and Fig. 2, the line shift coefficients for different compositions of the active medium of the CO_2 lasers. Thus for mixtures CO_2: N_2: He in the 1:1:6, 1:5:2, and 1:2:3 ratios, respectively, the line shift coefficient is about 0.006. . .0.010 $cm^{-1} \cdot atm^{-1}$.

The computational results for transmission of vertical atmospheric column are presented in Table II for some series of lasing frequencies of the CO_2 laser. The values of the collisional shift coefficients of absorption lines of atmospheric CO_2 (β_{al}) and of lasing lines of laser (β_{11}) which were used in calculations, are indicated in the second and third columns of Table II. The calculations were performed for summer in mid-latitudes under assumption that the active medium was at pressure about 1 atm.

As can be seen from Table II an account of the line collisional shifts yields 1.5–2 times increase of transmission of the vertical column of the atmosphere, though in some cases (for the lines 9P18 and 10R20) the atmospheric transmission remains practically unchanged. Enhanced transmittance is caused by the drift of the center of the lasing line of the laser off the center of the resonance absorbing line of atmospheric CO_2. In so doing, the contribution of absorption by the CO_2 molecules into the monochromatic absorption coefficient k_{CO_2} changes insignificantly (by about 5%) in the surface layer while in the upper layers of the atmosphere it decreases by a factor of 2–3.

This tendency in altitude behavior of the monochromatic absorption coefficient can be distorted due to absorption by other atmospheric components and closely located absorption lines due to "hot" transitions. Thus for the line 10R22 (ν = 997.214 cm^{-1}) k_{CO_2} decreases by a factor of 2.5 at a height of 10 km, whereas for the lines 10P20 and 9P22 noticeable changes in k_{CO_2} can be detected only at heights above 10 km.

TABLE II. Transmission of vertical column of the atmosphere.

Lasing frequency (cm^{-1})	Line shift coefficient due to absorption β_{al} cm^{-1}	Lasing line shift coefficient β_{11} cm^{-1}	Transmission
1050.44(9P16)	–	–	0.084
	0.006	0.009	0.167
1048.66(9P18)	–	–	0.036
	0.013	0.009	0.001
1046.854(9P20)	–	–	0.131
	0.006	0.007	0.203
1045.022(9P22)	–	–	0.224
	0.013	0.0084	0.352
1075.988(9R16)	–	–	0.168
	0.02	0.008	0.303
1077.302(9R18)	–	–	0.193
	0.015	0.0075	0.335
1078.59 (9R20)	–	–	0.190
	0.02	0.0094	0.354
945.980(10P18)	–	–	0.290
	0.013	0.007	0.420
944.195(10P20)	–	–	0.332
	0.013	0.006	0.422
	0.013	0.018	0.458
942.383(10P22)	–	–	0.326
	0.013	0.007	0.450
975.930(10R20)	–	–	0.106
	0.02	0.01	0.127
977.214(10R22)	–	–	0.291
	0.02	0.009	0.418

We have also performed, computer calculations of the atmospheric transmission at higher pressures of the active medium of laser (in particular, at $P = 2$ atm). As a rule, in this case the atmospheric transmission increases not so noticeably though in the particular cases the effect is appreciable. Thus for the line 9*P*16 the atmospheric transmission of the vertical path (~ 0.08 at low pressures of the active medium) increases up to 0.17 and 0.34 at pressures of 1 and 2 atm, respectively.

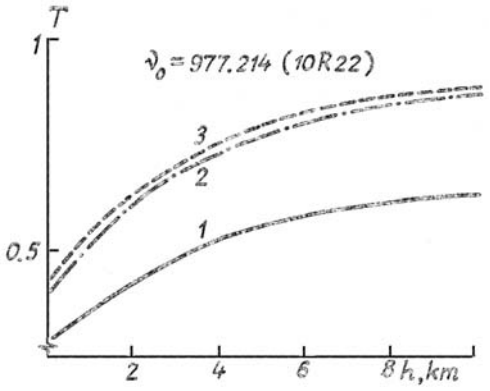

FIG. 3. Transmission of the atmosphere along a vertical path as a function of the lover endpoint height.

It is of certain interest to compare the value of the effect discussed above with estimations of enhanced transmission due to nonmonochromaticity of the lasing line of laser.[14] Figure 3 presents the calculational data on atmospheric transmission of vertical column as a function of lower endpoint height h of the path for monochromatic lasing line 10*R*22 of laser (curve 1) for the Gaussian lasing line of laser with a half–width of 0.012 cm^{-1} FWHM (curve 2), and for the monochromatic lasing line displaced at 0.009 cm^{-1} (curve 3). As can be seen from this figure, curves 2 and 3 are very close with each other for the line broadening and shift coefficients used in calculations. An account of nonmonochromaticity of a displaced lasing line of laser gives further, although insignificant, increase by 2–3% of calculated atmospheric transmission. Similar results we obtained for other lasing lines of the CO_2–laser.

The results that have been obtained here show that the discovered effect of the line collisional shift of CO_2 can have a marked effect on parameters of molecular absorption during propagation of the lasing lines of the CO_2 laser in the atmosphere. In addition the understanding of this mechanism of the atmospheric absorption allows the optimization of CO_2 laser based optical system to be performed by the displacement of the lasing lines of lasers into the atmospheric transparency microwindows with the help of variations in composition and pressure of an active medium. To solve such problems, subsequent theoretical and experimental studies of collisional line shifts depending on a buffer gas and thermodynamic parameters of the gaseous medium are needed.

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